AFOSR 69-2555TR

AD 695-073.

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I. INTRODUCTION

This final technical summary report covers the period of 16 December 1965 to 14 December 1967. The success which we have attained in the realization of our research objectives is demonstrated by the summary of accomplishments under this grant in Section II. Part A of that section describes the experimental results by topic. Part B is a list of publications sponsored by this grant (excluding those listed in the 1965 final report). Part C is a list of talks given and national and international meetings attended under the sponsorship of this grant. In Section III, we make recommendations for future work in this field.

II. SUMMARY OF ACCOMPLISHMENTS UNDER THIS GRANT TO DATE (1965-1967).

Part A. Description of results by topic

1. The main accomplishment of this program to date is that the elastic constants and their pressure and temperature derivatives have been measured on many specimens. The actual measured data are completed for polycrystalline Al_2O_3, a single crystal spinel ($MgO \cdot 2.6\ Al_2O_3$), single crystal garnet, polycrystalline Mg_2SiO_4, and polycrystalline ZnO. This is shown in Table 1. In addition, the data on polycrystalline CaO and polycrystalline BeO are partially complete. These data will provide future references for many thermodynamic considerations of

properties in the earth's interior.

2. The experimental approach we use allows us to measure the value of the bulk modulus K_o, and the derivative of the bulk modulus with pressure, K_o'. (Here the subscript zero means evaluated at zero pressure.) We have found that to a high degree of precision, K' is independent of pressure up to the limits of our experiments, 3 kb. We also find that if we assume that K' is independent of pressure at much higher pressures, we can predict the results of density pressure measurements obtained by other kinds of experiments. The basic for predicting experimental values is that since K is a differential of pressure with density, the assumption K_o' is a constant yields a differential equation which integrates to a particular ρ-P relationship. This is the Murnaghan equation of state, which contains only the two measured quantities K_o and K_o', and no arbitrary constants. As a consequence, our acoustic measurements have provided a method of tying into and calibrating shock-wave data measurements at very high pressures. This method of correlating shock data and acoustic data was not used before our work began. We therefore believe our work has had an impact on shock-wave analysis.

3. By using the equation of state resulting from the condition $K_o' =$ constant, we have been able to derive equations for the seismic velocity as a function of pressure, and the coefficient of thermal expansion as a function of pressure. Because of arguments discussed in Part 2 above, we believe that these equations are valid over pressure ranges of several hundred kilobars (in the absence of phase changes). These equations are

density, $$\rho/\rho_o = \left(1 + K_o' \frac{P}{K_o}\right)^{1/K_o'} \quad \text{(Ref. 2, p. 7)}$$

seismic parameter, $$\phi = \frac{K}{\rho} = \frac{K_o}{\rho_o}\left(1 + K_o' \frac{P}{K_o}\right)^{\frac{K_o'-1}{K_o'}} \quad \text{(Ref. 2, p. 7)}$$

thermal expansion, $$\alpha \cong \alpha_o\left(1 + K_o' \frac{P}{K_o}\right)^{-1} \quad \text{(Ref.10, p. 8)}$$

The important point about these equations is that the parameters ρ_o, α_o, K_o, and K_o' are all determined at very low pressures, so that values of constants, such as reported in Table 1, are sufficient to estimate the quantities ρ, ϕ, and α at very high pressures. These equations are useful to theories concerning the history and structure of planets. No claim is made for their being formally rigorous, but the equation

for ρ/ρ_o seems to be as accurate as the best available measured data; and if that equation is valid, the two equations which follow are also valid.

4. We have found extrapolation formulas for the elastic constants at very high temperatures. (This original work was not credited to this grant because it was done with equipment at Bell Telephone Laboratories while Dr. Soga was on leave from Lamont to Bell Labs. It has become very important to this grant.) According to our theory, as confirmed by experiments up to 1300°C, the variation of bulk modulus with temperature at high temperatures is given by

$$\frac{dK}{dT} = -\frac{\delta\gamma C_p}{V} \qquad \text{(Ref. 5, p. 7)} \quad \text{(Ref. 7, p. 8)}$$

where δ and γ are measurable constants, V is the specific volume, and C_p is specific heat. This expression predicts that dK/dT does not change very much with composition. This is demonstrated by measured values in Table 1. An important result of this work is that it allows one to predict the behavior of velocity with temperature in the mantle.

5. We can predict the variation of $(\partial T/\partial P)$ at constant $\phi = \sqrt{K/\rho}$ as a function of pressure and temperature at high pressures and temperatures. This results

from the extrapolation procedures outlined in (4) and (5) above. This parameter is very important in the estimates of thermal gradients in the mantle materials. As an example, the extrapolated values of $(\partial T/\partial P)$ at constant are given below in degrees/kilobar for the case of a garnet.

P \ T	$25^{\circ}C$	$500^{\circ}C$	$1000^{\circ}C$	$1500^{\circ}C$
0 kb	27	21	19	18
30 kb	26	20	18	17
50 kb	24	19	17	16
100 kb	23	18	16	15

We are able to predict the variation of the critical geothermal gradient (the gradient at which ϕ is constant with depth) on a given P-T profile. The P-T range available for this extrapolation extends to the limits of the upper mantle of the earth.

Part B. List of publications (excluding those listed in the 1965 final report) sponsored by this grant.

PUBLISHED:

1. "Temperature dependence of the velocity derivatives of periclase," J. Geophys. Res., 71, 3007-3012, 1966, by E. Schreiber and O. L. Anderson.
2. "Seismic parameter ϕ: Computation at very high pressure from laboratory data," Bull. Seismol. Soc. Am., 56(3), 725-731, 1966, by O. L. Anderson.

3. "A proposed law of corresponding states for Oxide compounds," J. Geophys. Res., 71, 4963-4971, 1966, by O. L. Anderson.
4. "Pressure derivatives of the sound velocity of polycrystalline forsterite with 6% porosity," J. Geophys. Res., 72, 760-764, 1967, by E. Schreiber and O. L. Anderson.
5. "Derivation of Wachtman's equation for the temperature dependence of elastic moduli of oxide compounds," Phys. Rev., 144(2), 553-557, 1966, by O. L. Anderson (submitted under Bell Labs byline).
6. "Pressure derivatives of elastic constants of single crystal MgO at 23°C and -195.8°C," J. Am. Ceram. Soc., 49, 404-409, 1966, by Orson L. Anderson (submitted under Bell Labs byline).
7. "High temperature elastic properties of polycrystalline MgO and Al_2O_3," J. Am. Ceram. Soc., 49, 355-359, 1966, by N. Soga and O. L. Anderson (submitted under Bell Labs byline).
8. "Variable air transformer for impedance matching," Rev. Sci. Instr., 37, 1625-1626, by P. Mattaboni and E. Schreiber.

IN PRESS:

9. "Elastic moduli of single crystal spinel at 25°C and to 2 kbar," J. Am. Ceram. Soc., by E. Schreiber.
10. "An equation for thermal expansivity in planetary interiors," J. Geophys. Res., by O. L. Anderson.
11. "Sound velocity in rocks and minerals," chapter in a book, Physical Acoustics, IVB, Academic Press, O. L. Anderson and R. C. Liebermann.
12. "Elastic constants of oxides used to estimate the properties of the Earth's interior," Proceedings--NATO Advanced Study Institute: on the Application of Modern Physics to the Earth and Planetary Interiors, 29 March-4 April, 1967, Newcastle upon Tyne, England, by O. L. Anderson and R. C. Liebermann.

Part C. List of talks sponsored by this grant

Presentation of contributed papers before the 1966 and 1967 April meetings of the American Geophysical Union. Invited seminars at Yale University, M.I.T., U.C.L.A., University of Hawaii, Rice University, California Institute of Technology, and Air Force Institute of Technology, Dayton, Ohio, and AFOSR, Washington, D. C.

Invited paper at NATO Conference on Application of Modern Physics to the Earth and Planetary Interiors, 29 March 1967, Newcastle.

Invited paper at fall meeting of the Basic Science Division of the American Ceramic Society, Pittsburgh, Pa., October 1965.

III. Recommendations for future work

The results described in the previous section indicate the desirability and the rewards of continuing our work and extending it to a new set of objectives.

OBJECTIVES

Part A. Continue the work of the previous grant (see objectives listed in proposals of 15 December 1965 and 15 December 1966).

1. Prepare and measure the sound velocities as a function of pressure and temperature on unmeasured oxide compounds and minerals: in particular, those oxides containing transition elements Fe, Mn, and Ni.
2. Estimate the limits on geothermal gradients in the earth's mantle from new and old data obtained from work on this grant.
3. Choose the experiments and interpret the results to bear upon current geophysical problems such as earthquake mechanisms, convection in the mantle, and seafloor spreading.
4. Find the thermodynamic variables in the neighborhood of phase changes.

Part B. Begin new work on the measurement of thermal expansivity as a function of pressure and temperatu

1. Measure the thermal expansivity in oxide compounds a a function of pressure at different temperatures.

Part C. Find practical ways of measuring the elastic constants and their pressure derivatives of the monoclinic crystal class

Part D. Exploit the spherical resonance technique for measuring elastic constants

1. Compute the expected behavior for spherical resonance for spheres made from nonisotropic substance.
2. Measure the shear velocity of small spheres as a function of temperature over wide temperatures.

Part E. Find suitable rock specimens for laboratory measurements which have come to the surface from deep in the earth's interior

Items 1, 2, and 3 of Part A above are extensions of our previous work. Part A4 has not been indicated before, so some brief comments will now be made. Suppose there is a phase change at pressure P*. Acoustic measurements will predict the volume at pressures above P* by the extrapolation techniques described. By using shock-wave techniques the volume above P* can be measured, and can be interpolated below P* to zero pressure. Thus one can estimate the volume change ΔV between the two phases above and be low the transition pressure. The product of the pressure and the ΔV is the change in enthalpy between the two phases. By using the condition that the free energy difference vanishes at the transition, and by exploring new (yet undefined) techniques for measuring the entropy difference at all pressures, one may hope to arrive at the basic information for thermodynamic constants relative to phase changes. This point should be explored theoretically and experimentally. Such information may possibly lea

to the prediction of phase changes.

Part B of OBJECTIVES concerns thermal expansivity. In the course of our work, we have found that the data on thermal expansivity are important to transform and interpret our acoustic data. We have measured our own thermal expansivity data as a function of temperature. Very little work has been done since the time of Bridgman on the measurement of thermal expansivity as a function of pressure. This work should begin. The relation between acoustic data and the α-P relationship is given by the third equation on page 3.

Part C of OBJECTIVES concerns the problem of making acoustic measurements on samples of low symmetry. The number of data which one must measure, on the basis of present theory, is formidable. The theoretical aspects of this problem should be considered in order to make an experiment program practical.

Part D of OBJECTIVES concerns the spherical resonance technique which has been exploited by Soga and Anderson (J. Geophys. Res., 72, 1733-1739, 1967) as a method for measuring small tektites on a NASA project. In the future, it may be useful for sound velocity measurements on small but rare minerals. It thus may be pertinent for the Apollo lunar material program, if that program ever materializes. However, we are concerned here with the use of spherical resonance to general problems in geophysics and rock mechanisms. One advantage of this method is that sphe can be prepared easily; while the main disadvantage is that the

theory has not been worked out for spheres of arbitrary crystal symmetry. We want to solve this important problem, so that we may be provided with a very powerful technique for dealing with small specimens. Lower symmetry causes mode-splitting, but so does asphericity of the specimen. These lead to departures from the isotropic case and must be distinguished from each other. The application pertinent to our work is the adaptation of the spherical resonance technique to determining the effects of temperature on sound velocity. It may also be feasible for use with pressure experiments as torsional mode should not be damped by fluid at high pressure. Thus we would expect to be able to measure the effect of pressure on the shear velocity of a small specimen.

Part E of OBJECTIVES concerns the acquiring of real material from the deep parts of the earth. Our program has, from the firs been designed to start from the simplest oxide compounds and grad ually work to more realistic components of the earth's interior. We are about ready to begin measurements on natural rocks such as eclogite, dunite, peridotite, pyroxinite, and their constituent minerals. The preliminary survey of work on these compounds is tabulated and discussed in a VESIAC State-of-the-Art Report, "Sound Velocities in Rocks and Minerals," (by O. L. Anderson and R. C. Liebermann, issued November 1966 by the University of Mich igan Geophysics Laboratory for ARPA). We are presently looking for suitable specimens for our existing techniques.

There are two field problems. First, we want to find the available rocks from the deepest regions of the earth--and for this we need to apply the techniques of geology; second, we want to select from these rocks those which are suitable for measurements by our techniques. This involves field trips, preferably with the help of a trained field geologist.

In the past eighteen months, we have gone on two field trips to find specimens using funds from this grant. We found an aphanitic nonvesicular basalt near Lava Falls, Grand Canyon. We We found some eclogites at the Mule Ear kimberlite pipe in southern Utah, which apparently were derived from great depth. This encourages us to seek our own specimens. We propose to look for suitable samples from three possible kinds of locations. First, xenoliths from volcanoes (such as found on Mauna Loa, Hawaii); second, ultrabasic rocks from orogenic zones (such as those occurring in the Franciscan formation of California), and third, ultrabasic rocks from cratonic zones (such as the Mule Ear diatreme, Utah.

Orson L. Anderson

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Principal Investigator

TABLE I. PHYSICAL CONSTANTS (Subscript T means isothermal; subscript S means adiabatic; subscript t means shear wave; subscript l means longitudinal). May 18, 1967.

Property		Units	Polyc. Al_2O_3	Polyc. MgO	S.C. MgO	S.C. α-Quartz	S.C. Spinel	S.C. Garnet	Polyc. Mg_2SiO_4	Polyc. ZnO
Density	ρ_o	gm/cc	3.972	3.5803	3.5833	2.6485	3.6193	4.1602	3.021	5.621
Thermal Expansivity	α	per deg x 10^6	16.3	31.4	31.2	35.4	15.2	21.6	24.0	15.0
Specific Heat	C_p	erg/g/°C x 10^{-6}	7.83	9.41	9.24	7.27	8.08	7.61	8.39	4.57
Shear Velocity	v_t	km/sec	6.373	5.954	6.043	4.092	5.645	4.762	4.359	2.803
Long. Velocity	v_l	km/sec	10.845	9.766	9.693	6.046	11.543	8.531	7.586	5.939
Molecular Weight	M/p		20.03	20.16	20.16	20.03	20.07	23.79	20.10	40.69
Specific Volume	V	cc/mole	5.13	5.63	5.63	7.56	5.27	5.72	6.65	7.24
Bulk Modulus	B_S	kb	2521	1717	1622	377	2020	1770	974	1394
Poisson Ratio	σ_S		0.236	0.203	0.182	0.077	0.260	0.274	0.254	0.357
Shear Modulus	G	kb	1613	1273	1308	444	1153	943	574	442
Bulk Modulus	B_T	kb	2505	1692	1599	374	2010	1757	967	1389
Poisson Ratio	σ_T		0.235	0.199	0.179	0.074	0.258	0.272	0.252	0.356
Pressure Derivatives (Ambient)										
$(\partial B_S/\partial P)_T$			3.98	3.92	4.49	6.4	4.18	5.43	4.8	4.78
$(\partial B_T/\partial P)_T$			3.99	3.94	4.52	6.4	4.19	5.43	4.8	4.78
$(\partial G/\partial P)_T$			1.76	2.63	2.54	0.45	0.75	1.40	1.1	-0.69
$(\partial \sigma_S/\partial P)_T$		per kb x 10^4	1.02	5.63	2.07	46.5	2.97	3.03	7.4	6.46
$(\partial v_t/\partial P)_T$		km/sec/kb x 10^3	2.21	4.35	3.96	-3.38	0.43	2.17	2.45	-3.19
$(\partial v_l/\partial P)_T$		km/sec/kb x 10^3	5.18	7.71	8.29	13.7	4.9	7.84	10.3	3.64
Temperature Derivatives (Ambient)										
$(\partial B_S/\partial T)_P$		kb/deg	-0.16	-0.13	-0.16	-0.10	-0.16	-0.20	-0.13	-0.13
$(\partial B_T/\partial T)_P$		kb/deg	-0.21	-0.21	-0.24	-0.11	-0.19	-0.24	-0.16	-0.15
$(\partial \sigma_S/\partial T)_P$		per deg x 10^5	1.0	2.7	1.5	7.1	0.2	0.02	1.0	-0.6
$(\partial G/\partial T)_P$		kb/deg	-0.18	-0.24	-0.21	-0.007	-0.10	-0.11	-0.10	-0.02
$(\partial v_t/\partial T)_P$		km/sec/deg x 10^4	-3.1	-4.8	-4.0	0.09	-2.8	-2.2	-2.9	-0.39
$(\partial v_l/\partial T)_P$		km/sec/deg x 10^4	-3.7	-5.0	-4.9	-2.7	-3.2	-3.9	-4.1	-1.9
Thermal Gradients										
$(\partial T/\partial P)_{v_t}$		°/kb	7.12	9.06	9.95	375	1.5	9.73	8.50	-81.5
$(\partial T/\partial P)_{v_l}$		°/kb	14.0	15.4	16.9	51.4	15.3	20.3	25.4	19.5
$(\partial T/\partial Z)_{v_t}$ (Plane)		°/km	1.83	2.58	2.83	145	0.42	2.38	2.87	-14.7
$(\partial T/\partial Z)_{v_l}$ (Plane)		°/km	3.59	4.39	4.81	19.7	4.31	4.96	8.56	3.56
$(\partial T/\partial Z)_{v_t}$ (sphere) = (plane) $-\frac{v_t/R}{(\partial v_t/\partial T)}$		°/km	5.05	4.53	5.21	74	3.58	5.73	5.23	-3.43
$(\partial T/\partial Z)_{v_l}$ (sphere)		°/km	8.19	7.45	7.91	23.2	9.97	8.42	11.46	8.46
Anharmonic Parameters										
Gruneisen: $\gamma = \alpha B_S V/C_p$			1.32	1.60	1.55	0.694	1.05	1.22	0.97	0.814
γ_t =			1.201	1.580	1.396	0.235	0.487	1.14	0.881	-1.254
γ_l =			1.528	1.683	1.721	0.604	1.191	1.96	1.656	1.188
γ_{LT} =			1.231	1.590	1.431	0.284	0.526	1.20	0.95	-1.132
γ_{HT} =			1.310	1.620	1.504	0.358	0.721	1.41	1.14	-0.440
$\delta^S = -(dB_S/dT)/\alpha B_S$			3.9	2.4	3.2	7.4	5.2	5.3	5.6	6.2
Debye Temperature θ =		°K	1030	931	941	572	916	745	648	410

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

Lamont Geological Observatory of Columbia University
Palisades, NY 10964

2a. REPORT SECURITY CLASSIFICATION

UNCLASSIFIED

2b. GROUP

3. REPORT TITLE

MEASUREMENT OF P AND S SOUND VELOCITIES UNDER PRESSURE ON LABORATORY MODELS OF THE EARTH'S MANTLE

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

SCIENTIFIC -------- FINAL

5. AUTHOR(S) (First name, middle initial, last name)

Orson L. Anderson
Edward Schreiber

6. REPORT DATE

16 December 1967

7a. TOTAL NO. OF PAGES

12

7b. NO. OF REFS

12

8a. CONTRACT OR GRANT NO

AF49(638)-1355

b. PROJECT NO

9731

c.

627010

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

AFOSR 69-2555TR

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES

Tech, Other

12. SPONSORING MILITARY ACTIVITY

Air Force Office of Scientific Research
1400 Wilson Boulevard (SRPG)
Arlington, VA 22209

13. ABSTRACT

The techniques of ultrasonic interferometry were used to measure the elastic wave velocities as a function of pressure and temperature for many minerals: polycrystalline Al_2O_3, a single crystal spinel ($MgO \cdot 2.6Al_2O_3$), a single crystal garnet, polycrystalline Mg_2SiO_4, and polycrystalline ZnO. The pressure derivatives were measured to 2 kb at room temperature, and the temperature derivatives were measured at 1 atm. The determination of the bulk modulus (K_o) and its pressure derivative (K_o') near zero pressure enables us to extrapolate the acoustic data and to compare it with static and shock-wave compression data at much higher pressures. The assumption that K_o' = constant over large ranges of pressures leads to convenient expressions for the density, the seismic parameter, and the thermal expansivity as a function of pressure; these equations are useful to theories concerning the history and structure of planets. New extrapolation formulas based upon the laboratory data allow us to predict the behavior of the elastic constants at high temperature. The combination of the pressure and temperature derivatives of the elastic wave velocities lead to expressions for the critical thermal gradients which can be compared to the actual geothermal gradient.

DD FORM 1 NOV 65 1473

UNCLASSIFIED

Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Sound velocities						
Earth's mantle						
Acoustic measurements						
Rocks and minerals						